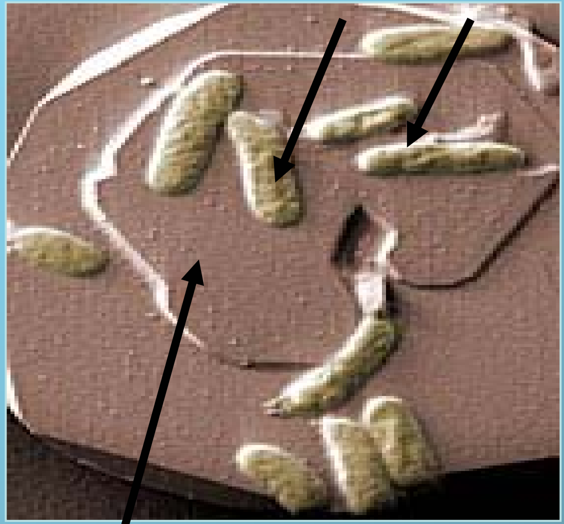
2004 APS Users Meeting Workshop

Future Directions in Synchrotron Environmental Science

Organizers: S. Sutton (U. Chicago), K. Kemner and S. Kelly (ANL-ER)

Microbe-Mineral Interactions

Shewanella



Tabular hematite (Fe_2O_3)

(J. Fredrickson, PNNL)

Remediation of Contaminated Groundwater

(Bangladesh; S. Fendorf, Stanford U.)

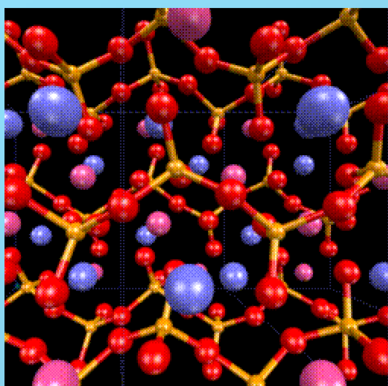
Environmental Science and Synchrotron Radiation

Research activity is driven by the need to understand how to remediate contaminated environmental materials

Synchrotron radiation plays a major role for the following reasons:

- **Complexity of environmental materials**
- **Presence of water and gases in environmental systems**
- **Need for molecular level information on speciation of contaminants**
- **Importance of interface structure on reactivity**
- **Presence of biota in environmental systems**
- **Value of molecular scale information in developing and evaluating remediation technologies**

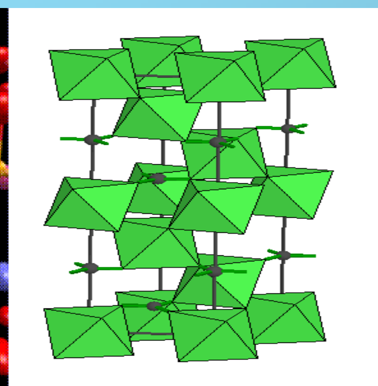
Atomic



- XRF
- XPS
- XAS

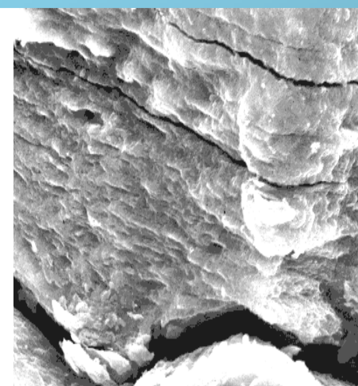
Requires synchrotron radiation.

Molecular



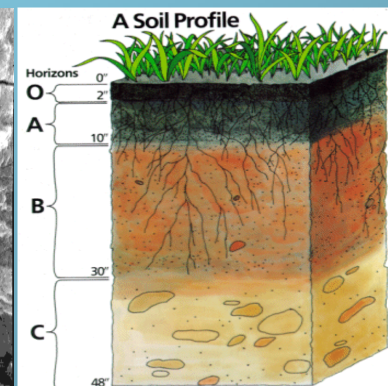
- XRD
- TGA
- FTIR
- DRS

Microscopic



- Enhanced Visual Analysis:
  1. SEM
  2. TEM
  3. AFM

Macroscopic



- Field Plots
- Equilibrium Studies
- Kinetic Studies
- Extractions

Field

- Visual/ Intuitive Insight
- Field Plots

K. Scheckel (EPA); Adaptation from Bertsch and Hunter, 1996.

2004 APS Users Meeting Workshop

Future Directions in Synchrotron Environmental Science

Agenda

Overview of Synchrotron Environmental Science	**Ken Kemner** (ANL)
How Do Metal-Reducing Bacteria Deal with Solid Phases?	**Jim Fredrickson** (Pacific Northwest National Laboratory)
Surface Complexation Models of Metal Cation Adsorption onto Bacterial	**Jeremy Fein** (University of Notre Dame)
Bioremediation of U Contaminated Subsurface Environments and the Role of Synchrotron-based X-ray Absorption Measurements	**Shelly Kelly** (Argonne National Laboratory)
Application of Synchrotron Radiation Based Techniques to the Biogenic Oxidation of Manganese	**Sam Webb** (Stanford University)
Environmental Science using the PNC-CAT Microprobes and Possible Future Directions	**Steve Heald** (Pacific Northwest National Laboratory)
Mineral-Water Interface Studies	**Tom Trainor** (University of Alaska)
Elemental, Chemical and Structural Characterization of Mineral-Water Interfaces with X-ray Scattering Techniques	**Paul Fenter** (ANL)
Correlating Metal Speciation in Soils to Risk	**Kirk Scheckel** (Environmental Protection Agency-Cincinnati)
Impact of Redox Disequilibria on Contaminant Transport and Remediation in Subsurface Systems	**Robert Ford** (Environmental Protection Agency-Oklahoma)
Resolving Biogeochemical Processes of Metals within Physically and Chemical Heterogeneous Media	**Scott Fendorf** (Stanford University)
Workshop Summary	**Paul Bertsch** (University of Georgia/SREL)

Scientific Topics

Microbe-mineral interactions

- Charge transfer reactions
- Metal binding mechanisms in microorganisms

Mineral surface structure-reactivity relationships

- Molecular-level structural effects of hydration
- Sorption processes on mineral surfaces in presence of surface modifiers (water, biofilms and organics).

Fate, transport and bioavailability of contaminants in ground water plumes

- Radionuclides from leaking high level waste tanks
- Natural heavy metal enrichments

Remediation technology development

- Bioremediation of reducible metals and radionuclides
- Phyto-remediation
- Reactive barriers
- Role of low abundance phases and preferential flow

Microbe-Mineral Interactions: How Do Bacteria Deal with Solids? - J. Fredrickson, PNNL

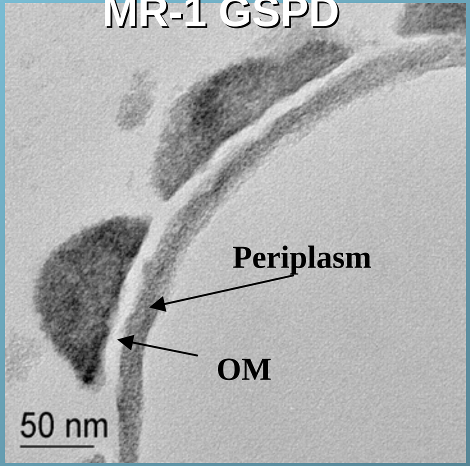
Significance

- Contaminant transport and remediation
- Central to planetary biogeochemical cycles
- Rock weathering, soil develop., water quality
- Reactive mineral formation & biocorrosion
- Early form of respiration on earth
- Energy for microbial lithotroph metabolism

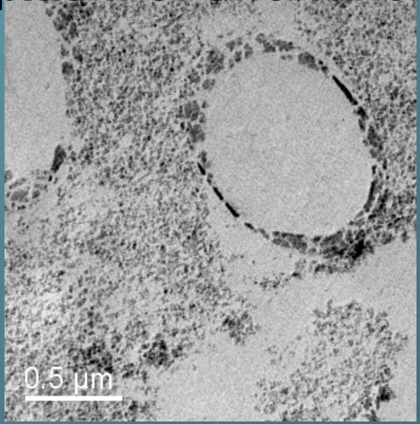
Opportunities for new experimental and computational capabilities

- High resolution microscopies, spatially specific spectroscopies, and new imaging techniques
- Fundamental modeling of protein and mineral structures and their chemical dynamics
- Characterization and study of complex environmental surfaces and phases

Reduction of TcO_4^- by MR-1 GSPD



UO_2 Accumulates in the Periplasm of *Shewanella*



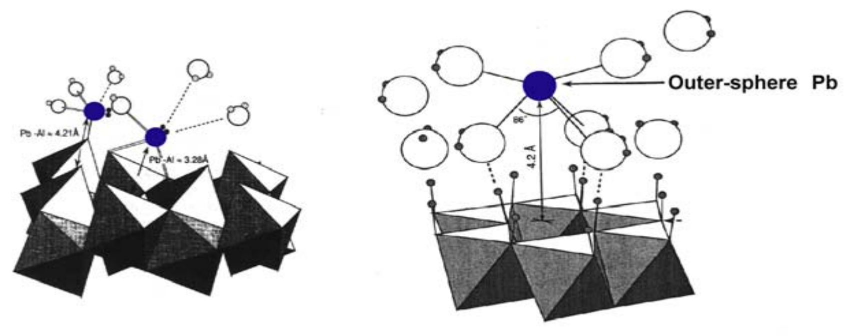
Mineral Surface Structure and Reactivity

T. Trainor (U. Alaska) et al.

Mineral surface reactivity is dictated by structure and composition
(sorbate binding mode; crystal face specificity)

Key variables/processes influencing structure

- **Bulk structure and composition**
- **Surface orientation**
- **Environment (H_2O, pH etc.)**
- **Chemical modification (heter. redox, dissolution/leaching, coatings)**



J. Bargar, *et al.* (1997) *J. Colloid Inter. Sci*. **185,** 473-492.
J. Bargar, *et al.* (2004) *Langmuir* **20,** 1667-1673.

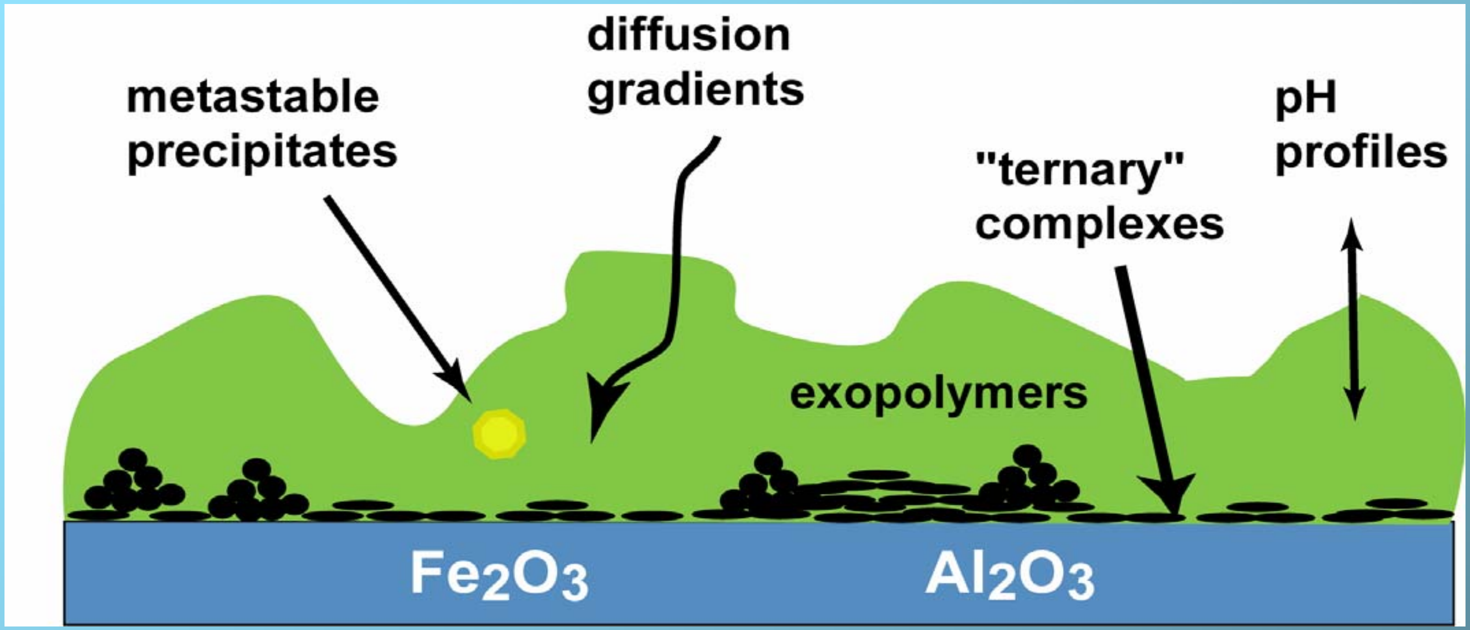
Approach

- **Investigate structure/reactivity in well constrained model systems**
- **Incrementally increase complexity and number of variables**

Goal

- **Obtain results that can provide molecular scale interpretation of macroscopic reactivity**
- **Test theoretical/mechanistic modeling approaches**

Surface Coatings: Biofilms and NOM



Mineral surfaces are coated with organic material in aquatic systems

- **Bacterial surfaces, associated exopolymers and other “natural organic matter” contain multiple functional groups available for metal binding.**
- **Do metabolically active bacteria “mineralize” contaminants?**
- **How reactive is the “organic coating” component?**
- **Does the presence of coating alter the intrinsic reactivity of the surface?**

Challenges

Hydrated Surface Structures (CTR)

- Expand range of bulk structures, compositions and surface orientations
- Structure of interfacial water

Surface Reactivity (CTR,GI-XAS, XSW)

- Test mechanistic predictive models by investigation of a range of sorbates on well defined surfaces
- Reactivity of surface defects
- Physical influences on surface speciation (temp, wet/dry)

Surface Coatings / Surface Reacted Layers (XRD, XSW, GI-XAFS)

- Growth modes of inorganic coatings
- Binding mechanisms of NOM/bacteria
- Direct study of micro-environments
- Formation of surface leached layers
- Reactivity of composite systems

Heterogeneous redox processes

- Impact on structure and reactivity
- Rates and mechanisms

Systematically increasing system complexity will provide insights into factors that control chemistry of "complex" natural interface systems.

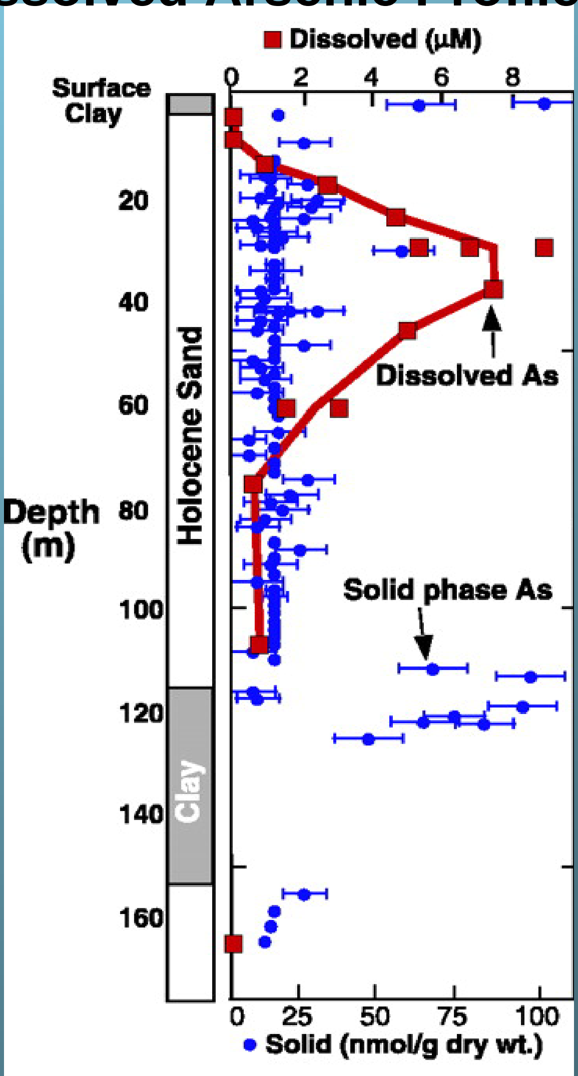
Heterogeneity in Biogeochemical Processes

S. Fendorf (Stanford U.) et al.

Bangladesh: Largest Mass Poisoning in History - Arsenic in Drinking Water

Average Well-Depth: 30 m

Dissolved Arsenic Profiles



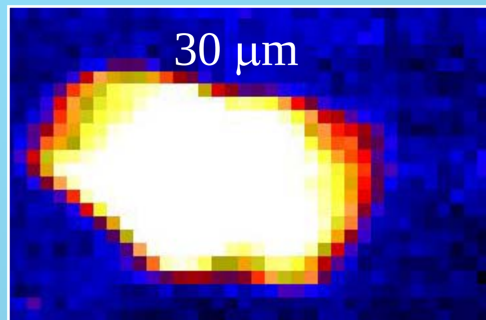
Remnant and Intact Arsenic Sulfides

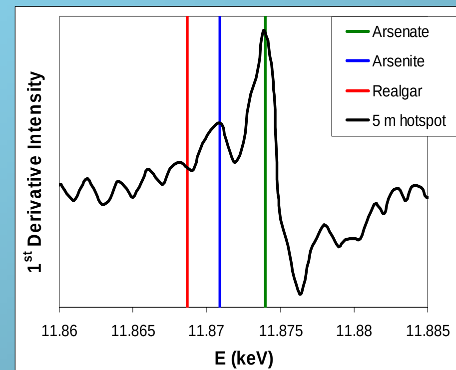
Arsenic microdistributions

Micro-XAFS

Depth

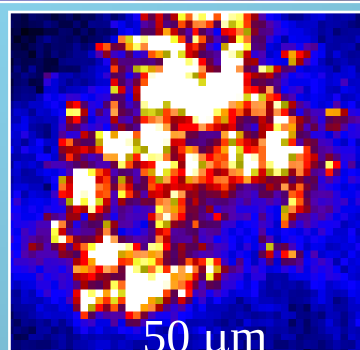
< 20 m

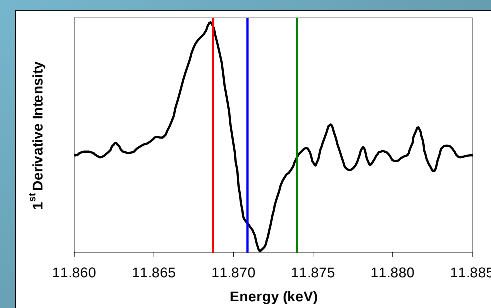




Arsenate/ arsenite

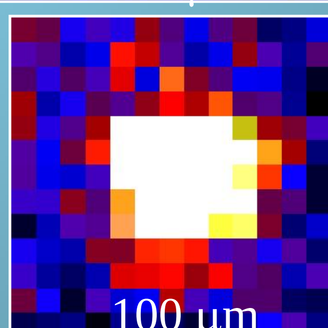
20-50 m

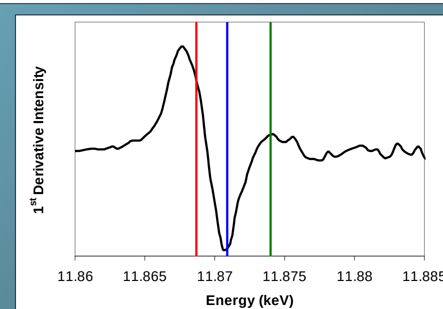




As-sulfide

>50 m

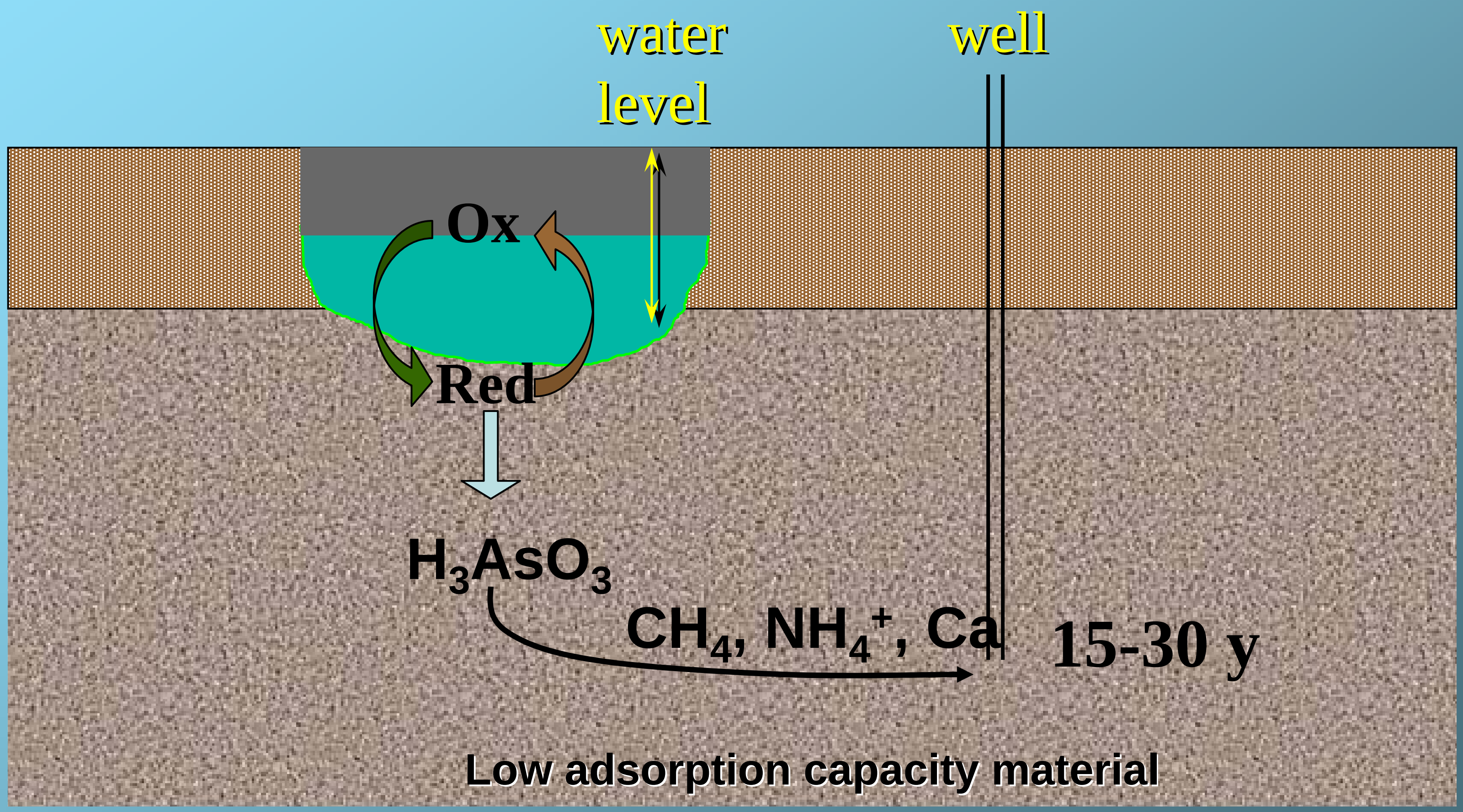




As-sulfide

Current Hypothesis

Near-surface liberation coupled with transport



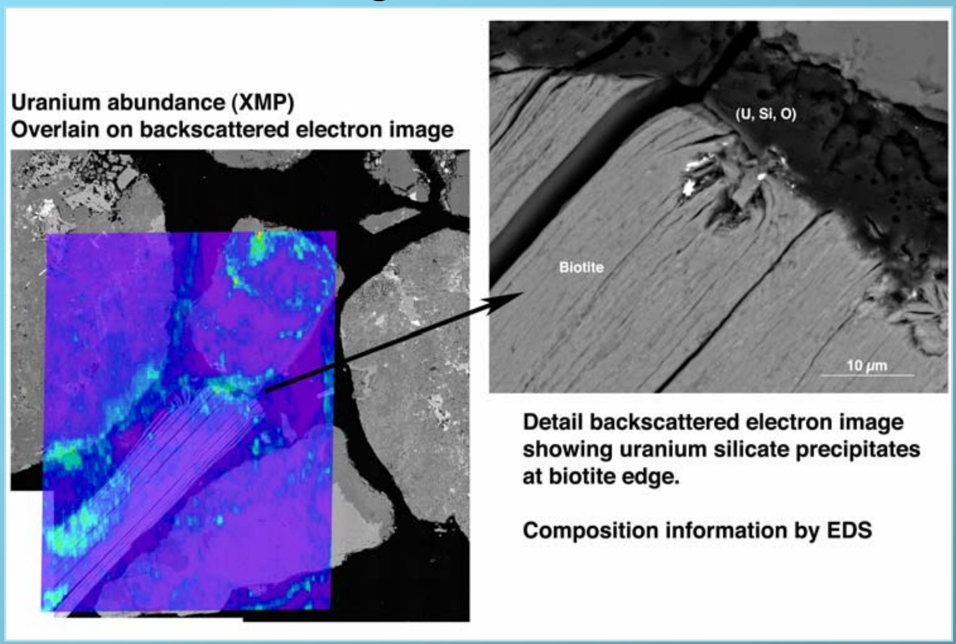
Future Directions and Needs

- **Studies encompassing physical, biological, chemical processes of natural environments**
- **Assessment of micro-scale heterogeneity in biogeochemical cycles**
- **Resolving points/areas of biological and chemical activity**

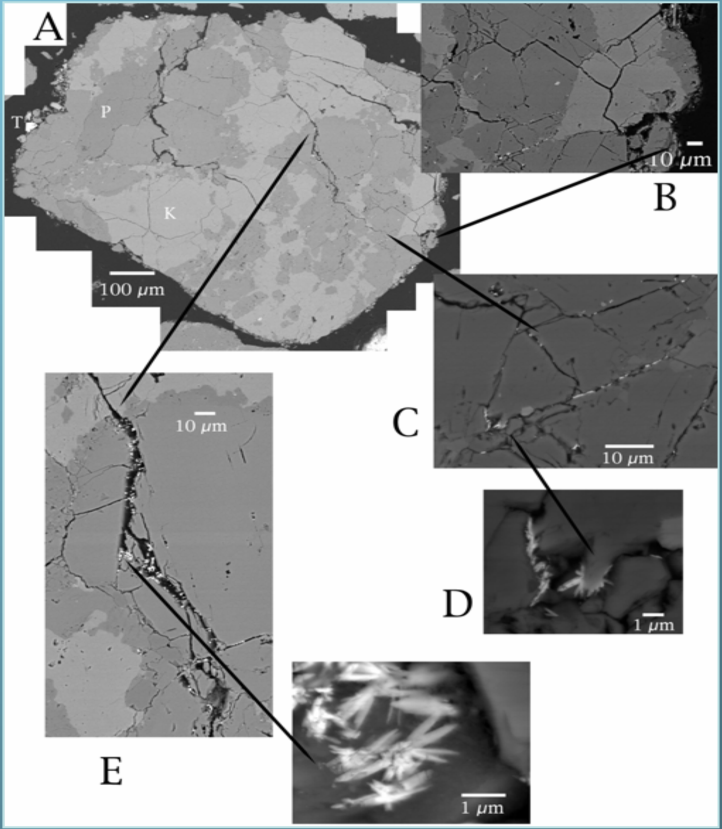
Hanford's B-BX-BY Tank Farm: Uranium Fate

S. Heald (Sector 20) and colleagues at PNNL and Stanford

XRM and SEM Analyses of U(VI) Containing Hanford Sediment



U(VI) Microprecipitates within Fractures of Quartz and Feldspar



Summary of B-BX-BY Uranium Work

- XAFS and micro-diffraction important for determining uranyl phase and to constrain kinetic modeling
- Boltwoodite is likely the dominant precipitated phase
- Unique micro-environment leads to enhanced precipitation and entrainment of U in cracks
- Dissolution studies indicate current conditions reasonably stable (should limit the infiltration of meteoric water)

Impact of Redox Disequilibria on Contaminant Transport and Remediation in Subsurface Systems – *R. Ford (EPA) et al.*

EPA Research in Support of Superfund and RCRA
Ground Water Remediation

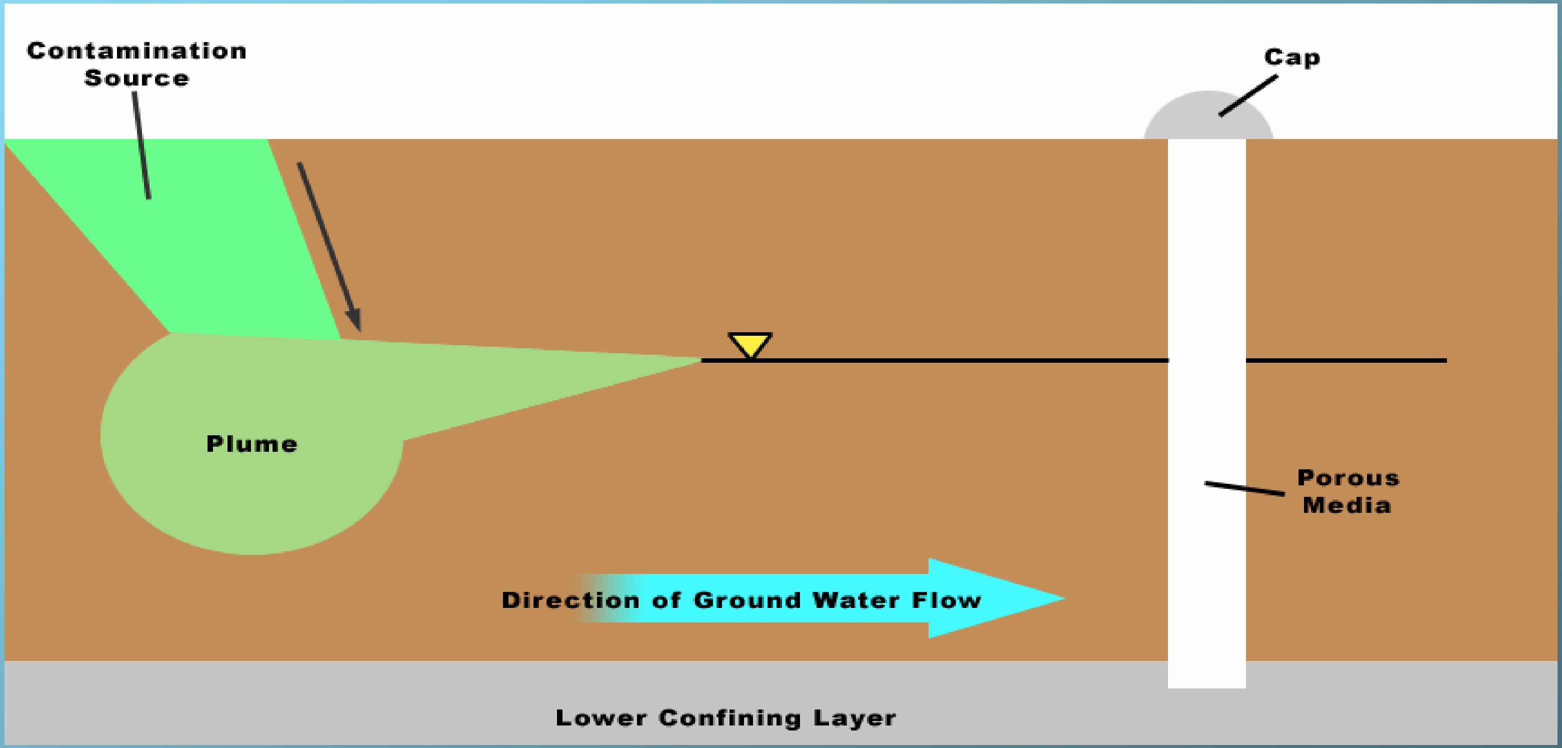
Goal:
Remediation of inorganic contaminants in ground water

Technology:
In-situ Permeable Reactive Barriers
Monitored Natural Attenuation (MNA)

Information needs:
Mode of contaminant immobilization
Stability of immobilized contaminant

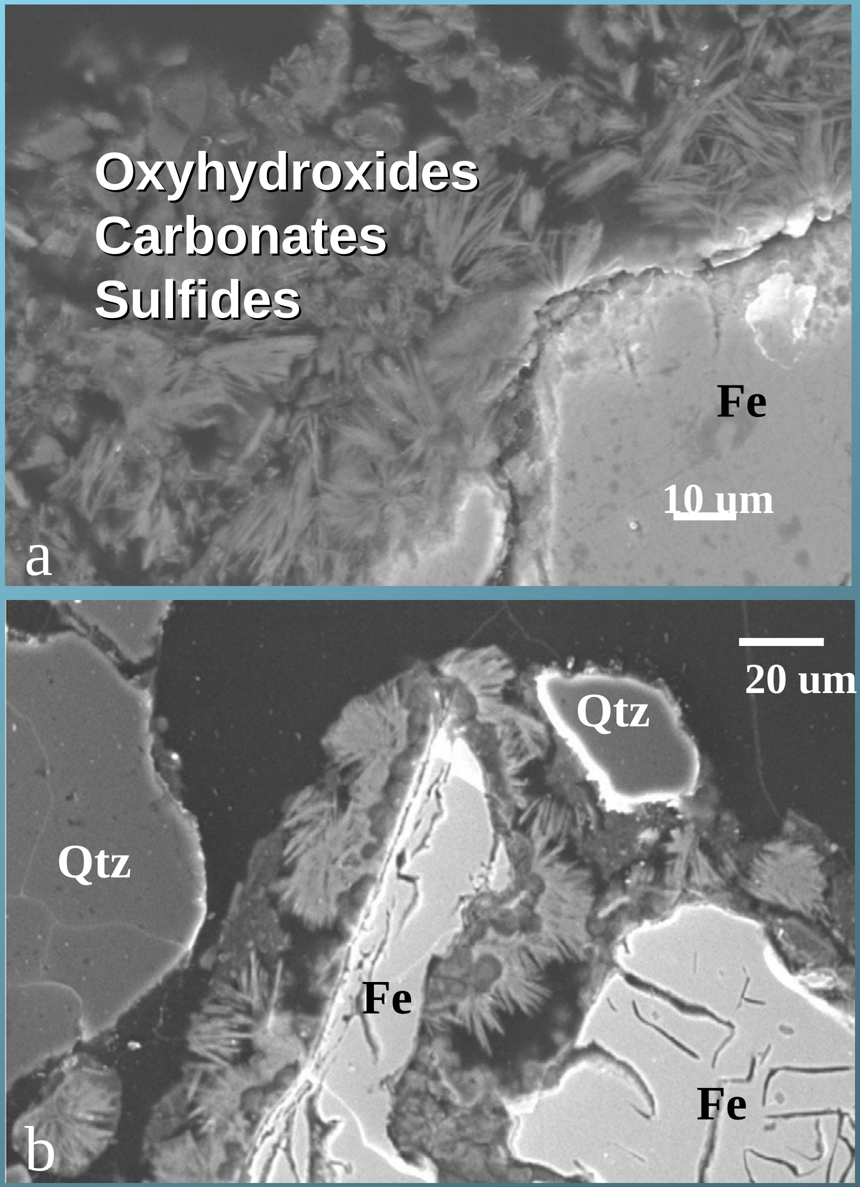
Permeable Reactive Barrier Research

- A permeable zone creating a reactive treatment area oriented to intercept and remediate a contaminant plume
- Removes or transforms contaminants from groundwater flow system by chemical or biological processes



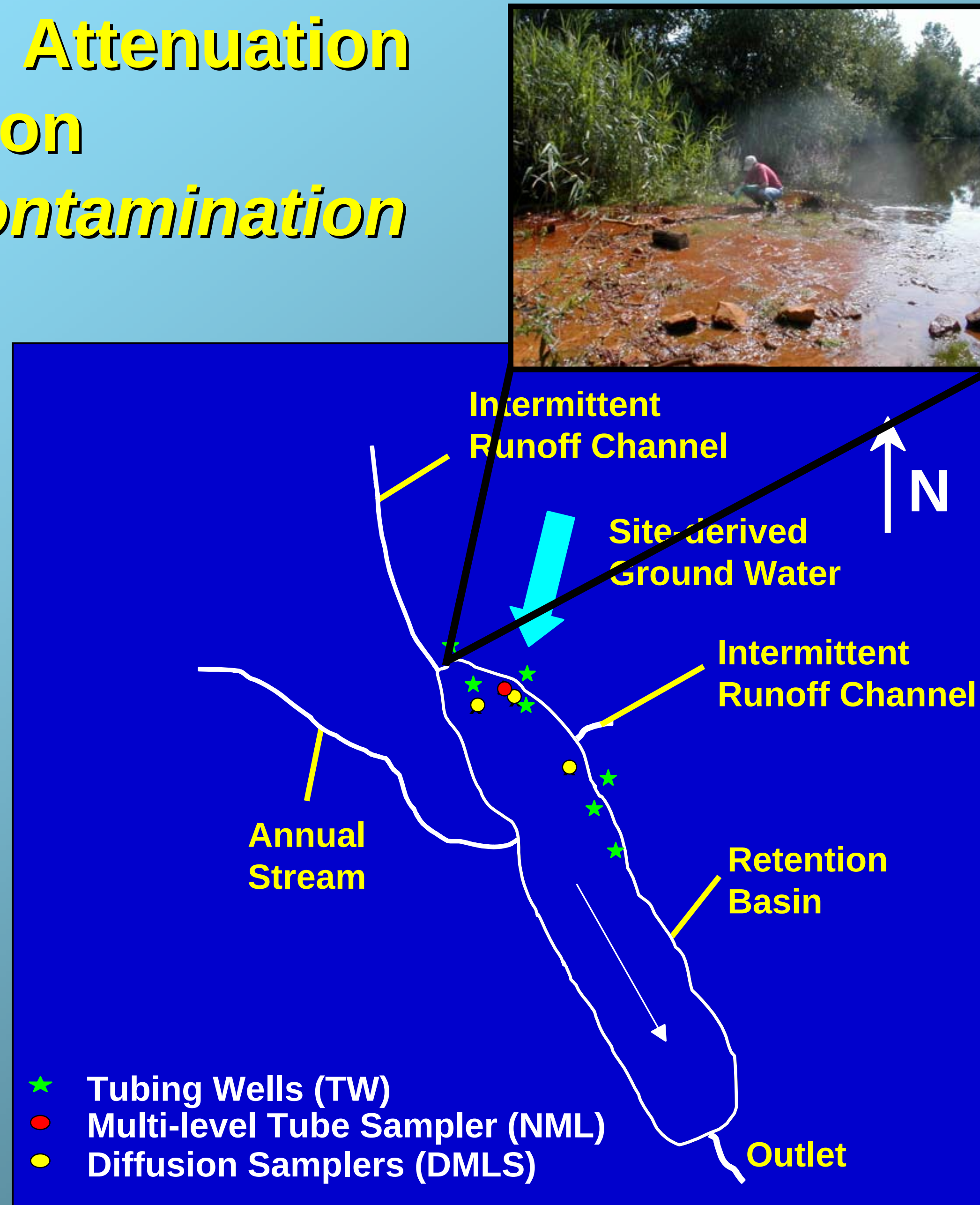
Fe Corrosion – Contaminant Uptake

- Pore infilling rates
- Changes in reactivity during corrosion
- Contaminant speciation relative to mineralogy of corrosion products



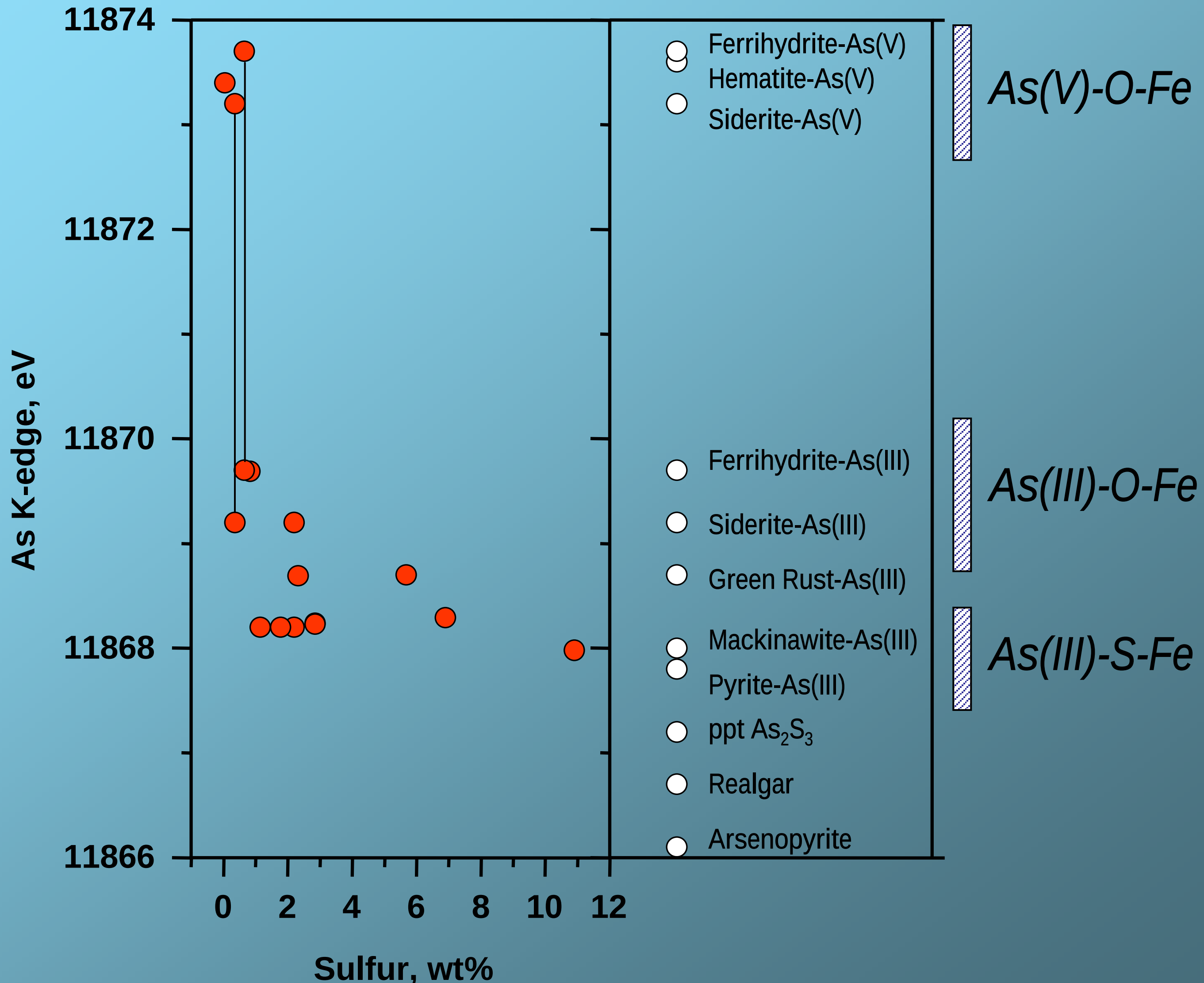
Monitored Natural Attenuation Evaluation
Site of Arsenic Contamination

- As-contaminated ground water
- Discharge of ground water to retention basin
- Fate of As linked to Fe-bearing minerals
- Laboratory studies needed to develop methods to speciate solid phase arsenic and to establish the reversibility (mobilization potential) of arsenic partitioned to soil and sediment materials



Arsenic Speciation in Sediments

- ***Pure arsenic sulfides are not forming.***



Future Directions

- Real samples: intermediate contaminant concentrations in high background matrix is the rule
- Poorly crystalline materials are common in contaminated systems (reactivity issues)
- Protocols for discerning processes at field scale (data scaling)
- Need to couple structural data with observed chemical reactivity
- XAS particularly valuable

\- Confirmation of mechanistic data from laboratory studies – building block for reactive transport modeling

\- Speciation of elements in contaminated media

\- Validation of macroscopic tests used to assess contaminant speciation, e.g. ‘selective’ extractions

Future Directions Summary (Science)

- Define electron transfer mechanisms between microbes and minerals; cell wall chemistry
- Improved extrapolation of laboratory results to natural systems
- Improved understanding of coupled physical, biological, chemical processes in natural environments
- Expanded knowledge of mineral surface properties: bulk structures, compositions, orientations, natural solids
- Experimental tests of mechanistic predictive models of sorption
- Binding mechanisms of NOM/bacteria
- Impact of heterogeneous redox reactions on surface structure and reactivity
- Assessment of microscale heterogeneity in biogeochemical cycles
- Validation of macroscopic tests used to assess contaminant speciation
- Reactivity of poorly crystalline materials

Future Directions Summary (Technical)

- Advances in high resolution microscopies, spatially specific spectroscopies, and new imaging techniques
- Continued improvement in spatial resolution; easily varied beam-size from mm to nm
- Wider operating energy range (~simultaneous light and heavy element analysis)
- Multiple-combined techniques in single instrument
- Quick or slew scanning for microspectroscopy
- Efficient detectors for improved detection limits
- Seamless integration of scattering and spectroscopy
- Improved ability for surface studies on small samples/select regions using microbeam techniques
- Dedicated ancillary facilities for specimen preparation and characterization

Study of Live Plant at Sector 20

K. Scheckel, EPA

Workshop Summary and Discussion

- **Synchrotron-based X-ray techniques have emerged as very important tools for examining complex environmental samples to provide insights into the hydrobiogeochemical processes that control the fate, transport, and bioavailability of contaminants and nutrients.**
- **Synchrotron environmental science (SES) user community has experienced dramatic growth over the past decade and the future growth should significantly increase the APS user community.**
- **SES user community has specialized requirements for instrumentation and sampling preparation/characterization apparatus.**
- **Nature of the samples can vary significantly as do requirements for handling and preparing these samples under carefully controlled environmental conditions.**
- **These specialized needs and flexibility requirements suggest science-focused facilities/beamlines should be considered in addition to more distributed resources.**

Need for Facilities Dedicated to Environmental Science

- **Environmental materials, fragile and susceptible to alteration under ambient conditions, must be studied *in situ* or soon after extraction.**
- **Advances require application of a variety of techniques over a wide range of spatial scale (<μm to >mm).**
- **Demand for access to microscale analytical techniques dedicated to environmental science research is increasing rapidly. There is a need for additional resources for single experiment, community access.**
- **Institutions with mature environmental science research programs require extended access, currently unavailable.**

Synchrotron Environmental Science at the APS

- **Currently conducted as small percentages of ~ dozen stations (no dedicated stations)**
- **Techniques include: XAFS, XRF, XRD, XSW, tomography (most over wide spatial scale range)**
- **SES beam time allotments are oversubscribed (~2x)**
- **Other DOE synchrotrons have environmental science dedicated beamlines** (e.g., X27A @ NSLS, 11-2 @ SSRL, 11.0.2 @ ALS)

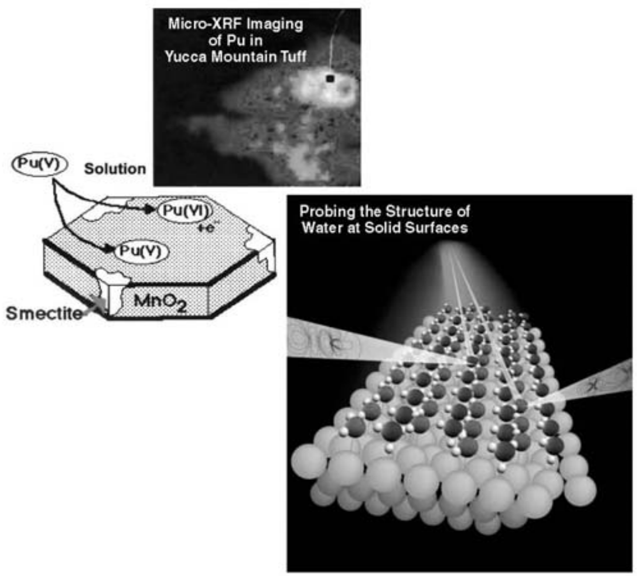
EnviroSync

- "Grass roots" organization of environmental scientists who use synchrotron radiation or have an interest in the application of synchrotron radiation to the environmental sciences
- Grew out of workshops on "Molecular Environmental Science" held in 1995 and 1997, organized by G. Brown, Jr., sponsored by DOE-Chemical Sciences
- Goals
  - Facilitate the use of synchrotron radiation by environmental scientists
  - Aid in the planning and development of beamlines
  - Inform environmental scientists about activities and developments in the field of synchrotron radiation applications in environmental science
  - Advocate synchrotron-based environmental science activities to federal agencies
- Website: www.envirosync.org (links to info on US facilities)

SLAC-R-704

2003 Report of EnviroSync – A National Organization of Environmental Science Users of Synchrotron Radiation Sources

Molecular Environmental Science: An Assessment of Research Accomplishments, Available Synchrotron Radiation Facilities, and Needs



Prepared in part for the Department of Energy under contract DE-AC03-76SF00515

Stanford Linear Accelerator Center
Stanford Synchrotron Radiation Laboratory
Stanford University, Stanford, California 94309

Molecular Environmental Science:
An Assessment of Research Accomplishments, Available Synchrotron Radiation Facilities, and Needs

Prepared on behalf of *EnviroSync* by

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Executive Summary

Synchrotron-based techniques are fundamental to research in *Molecular Environmental Science* (MES), an emerging field that involves molecular-level studies of chemical and biological processes affecting the speciation, properties, and behavior of contaminants, pollutants, and nutrients in the ecosphere. These techniques enable the study of aqueous solute complexes, poorly crystalline materials, solid-liquid interfaces, mineral-aqueous solution interactions, microbial biofilm-heavy metal interactions, heavy metal-plant interactions, complex material microstructures, and nanomaterials, all of which are important components or processes in the environment. Basic understanding of environmental materials and processes at the molecular scale is essential for risk assessment and management, and reduction of environmental pollutants at field, landscape, and global scales.

One of the main purposes of this report is to illustrate the role of synchrotron radiation (SR)-based studies in environmental science and related fields and their impact on environmental problems of importance to society. A major driving force for MES research is the need to characterize, treat, and/or dispose of vast quantities of contaminated materials, including groundwater, sediments, and soils, and to process wastes, at an estimated cost exceeding 150 billion dollars through 2070. A major component of this problem derives from high-level nuclear waste. Other significant components come from mining and industrial wastes,

EnviroSync Recommendations

- ***Increase Operations Funding for Existing Beam Line Stations***
- ***Increase Beam Line Station Availability for MES Activities***
  - *Redirect Existing Beam Line Stations*
  - *Plan for New Beam Line Stations*
  - *Enhance Access to Existing Innovative Beam Line Stations*
- ***Increase Funding for Essential Equipment and Sample Handling Facilities***
- ***Survey the Environmental Science Community to Determine Highest Priorities and Needs***